

Airborne, in Situ and Laboratory Measurements of the Optical and Photochemical Properties of Surface Marine Waters

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LONG TERM GOALS

The principal long-term objectives of this work are 1) to uncover and quantify the primary factors controlling the spatial and temporal distributions of the light-absorbing (colored) constituents of dissolved organic matter (CDOM) in marine and estuarine waters, 2) to determine the impact of CDOM on the aquatic light field and remotely-sensed optical signals, 3) to examine the effects of photooxidation on the optical absorption and emission properties of this material, as well as the relationship between the loss of absorption (and fluorescence) by photooxidation and the yield of photochemical intermediates and products, 4) to develop and apply new techniques for determining the photoproduction rates of transient intermediates in natural waters. A combination of field and laboratory measurements are being employed to estimate the wavelength dependence of the rates of the photobleaching response and its relationship to organic carbon photooxidation and the production of photochemical intermediates in order to better understand the impact of photooxidation on marine carbon and trace element cycles and the optical properties of seawater.

OBJECTIVES

Our near-term objectives have been 1) to complete two research cruises in July and September of 1998 devoted to examining the seasonal dependence of CDOM absorption and emission in the Middle Atlantic, the contribution of CDOM to the aquatic light field, and the effects of stratification on the photodegradation of CDOM and on the vertical structure of the optical properties, 2) to begin developing a photochemical model for photobleaching based on an extensive laboratory study of CDOM photobleaching kinetics that employed both monochromatic and broad band light sources, 3) to develop and apply new techniques for determining the photoproduction rates of the hydroxyl radical (OH) and the hydrated electron ($e_{(aq)}^-$), and 4) to begin construction of a web site for archiving data collected on our past cruises, so that other researchers can have access to these data.

APPROACH

One seven-day cruise in July and one five-day cruise in late September 1998 were performed to examine the optical and photochemical properties of waters in the Middle Atlantic Bight and in the Delaware and Chesapeake Bays. Data obtained from these cruises included: 1) optical absorption spectra of CDOM

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using standard spectrophotometers and onboard, using a liquid capillary waveguide (September cruise; Eurico D'Sa); 2) continuous onboard fluorescence measurements of CDOM; 3) for selected stations, 3-D fluorescence spectra of CDOM; 4) particle absorption spectra using the filter pad method; 5) detrital absorption spectra using the methanol extraction method; 6) DOC concentrations; 7) in-water downwelling irradiance and upwelling radiance using a Biospherical Instruments MER (September cruise; L. Harding and M. Mallonee); 8) in-water downwelling irradiance in both the UV and visible using a Satlantic SPMR, and above-water irradiance and just below-surface upwelling radiance using the Satlantic surface reference (July cruise; W. Miller and R. Davis); 9) backscattering coefficients employing a Hydrosat 6 backscatter meter (in collaboration with R. Maffione; September cruise); 10) continuous surface chlorophyll fluorescence measurements; 11) pigments, nutrients and primary production at selected stations (September cruise; L. Harding and M. Mallonee); 12) sampling for laboratory photobleaching and photochemistry experiments.

Our approach for detecting and quantitating OH production employs the rapid reaction of OH with dimethylsulfoxide to produce quantitatively a methyl radical, which then reacts with an amino-nitroxide to produce a stable, O-methylhydroxylamine. Following derivatization with fluorescamine, this radical adduct is separated by reversed-phase HPLC and quantified fluorometrically. Unlike many previous OH detection methods, this method can be employed under both aerobic and anaerobic conditions and thus, can be used to test whether the presence of dioxygen is required for OH formation.

Our approach for detecting $e_{(aq)}^-$ production employs the rapid reaction of $e_{(aq)}^-$ with N_2O to produce OH, which can then be detected via the reaction scheme described above. We are also examining the production of other CDOM photoreductants by employing chlorinated hydrocarbons with differing one-electron reduction potentials. Photochemically-initiated reductive dehalogenation of these compounds by CDOM will lead to the production of a carbon-centered radicals that can be trapped by an aminonitroxide and quantified as described above.

Our approach to modeling the photobleaching data is to first develop a matrix of quantum efficiencies acquired from the monochromatic irradiations. Multiplication of this matrix by the measured irradiances of our broad band source will then generate a vector of rate constants that can be used to calculate the time dependence of the photobleaching response, which can then be directly compared with the broad band photobleaching data.

WORK COMPLETED

1. Over the last two years, five (very) large sets of in situ optical and (photo)chemical data, and two major sets of airborne optical data have been acquired for the Middle Atlantic Bight. The PI and his collaborators are currently processing and integrating these data in preparation for publication.
2. A complete set of laboratory photobleaching experiments has been performed using both monochromatic and broad band light. We are currently developing a model from this data that should allow us to predict, at least to first-order, environmental photobleaching rates and the effect of different light fields on the spectral dependence of the photobleaching.
3. A new, highly sensitive method for the detection and quantification of photochemically-generated OH, produced either in the presence or absence of dioxygen, has been developed and applied to the

formation of OH by isolated CDOM and in natural waters containing CDOM. This work was recently published in *Environmental Science & Technology*. A related technique, applicable to biological systems, was published in *Analytical Chemistry* as an accelerated article.

4. A new method for determining $\epsilon_{(aq)}^-$ was developed and used to determine the wavelength-dependence of the quantum yields for its production, both in solutions of fulvic acids and in natural waters. This work is being prepared for publication. We are now proceeding with the mapping of the photoreducing “potential” of CDOM using a series of chlorinated compounds.

RESULTS

Although much of the data from the newer field work is still being processed, a preliminary analysis appears to support the conclusion reached in earlier field studies, namely that, in surface waters by late summer, photobleaching can significantly reduce light absorption by CDOM in surface waters and alter the relationship between absorption and DOC concentration due to the photodegradation of CDOM to uncolored DOC and dissolved inorganic carbon. Thus, stratification of the water column during the summer months appears to “trap” CDOM in a shallow mixed layer where it undergoes substantial photobleaching, whereas the CDOM in the deeper waters below the thermocline is protected due to the limited penetration of UV radiation.

Knowledge of the kinetics of the photobleaching response for CDOM is essential for an quantitative analysis of this problem. Thus, over the last year, we completed a detailed laboratory study of CDOM photobleaching using both broad-band and monochromatic light. The salient results are summarized below:

- Photobleaching exhibits biphasic kinetics with the lifetime of the faster component in the range of 10-30 hr and the lifetime of the slower component in the range of 100-3000 hr, depending on the wavelength of irradiation.
- The rate of absorption (and fluorescence) loss is greatest at the irradiation wavelength, although significant rates of loss are also observed outside the irradiation wavelength. Thus, irradiation with monochromatic light can produce photochemical “hole-burning” in the absorption and in the fluorescence excitation-emission matrix (EEM or 3-D) spectra of the CDOM. The loss of absorption at the irradiation wavelength is likely due to the direct photochemical destruction of the chromophore(s) absorbing at that wavelength, whereas the broad loss of absorption at the other wavelengths may be caused by reactions with secondary photochemical intermediates such as reactive oxygen species.
- The efficiency of both the primary and secondary bleaching decreases with increasing wavelength and is greatest in the UV-B and UV-A.
- The photobleaching kinetics are similar for CDOM from different sources.

Based on these results, we are currently attempting to develop a generalized spectral response function from which the environmental rates and spectral dependence of CDOM absorption (and fluorescence) loss can be predicted.

In applying the new method for OH detection, we have found that the photolysis of Suwanee River fulvic acid (SRFA) and CDOM in natural waters produces OH under both aerobic and anaerobic conditions. A linear relationship between SRFA concentration and OH production was observed under both aerobic and anaerobic conditions. The wavelength of the quantum yields for hydroxyl radical formation above ~310 nm were similar to those found previously by Mopper and Zhou, whereas the yields below ~310 nm were significantly smaller. Further experiments indicate that Fenton chemistry can account for only 30-40% of the total OH signal under aerobic conditions. The results indicate the presence of a dioxygen-independent pathway of OH production which is not due to nitrate or nitrate photolysis or photo-Fenton chemistry.

The carbon-centered radicals produced by reaction of the hydrated electron (formed by photolysis of ferrocyanide) with a series of chlorinated compounds have been trapped, separated and identified by HPLC and mass spectrometry. The reaction of N_2O with the hydrated electron to form OH, followed by the reaction of OH with dimethylsulfoxide to form a methyl radical which is subsequently trapped with an amino-nitroxide, has been used to obtain the wavelength dependence of the quantum yields for hydrated electron production by SRFA and CDOM in a number of natural waters. The ability of CDOM to reductively de-chlorinate a series of chlorinated compounds with differing one-electron reduction potentials is currently being examined.

IMPACT

Because CDOM dominates light absorption in the blue portion of the visible spectrum in surface coastal waters throughout much of the year, it directly impacts underwater visibility and the propagation of visible radiation in the littoral environment. These factors can affect the ability of the operational Navy to detect and identify submerged enemy ordnance and to perform their own operations discreetly in these environs. For these reasons, an understanding of the factors that control the spatial and temporal variability of this material and its impact on the optical properties of coastal waters should be of direct benefit to the Navy.

We have also developed several highly-sensitive methods to detect and quantify the production of transient intermediates in natural waters. Related methods, based on our earlier work, have been developed and applied to important biological problems such as the production of OH in mammalian cells (see references below).

RELATED PROJECTS

Over the past year, we have continued our collaborations with Dr. Larry Harding (University of Maryland) and with Dr. William Miller and Dr. John Cullen (Dalhousie University). These collaborations have brought additional expertise and field measurement capabilities to bear on the goals of determining the levels of CDOM and photochemical fluxes remotely via airborne and satellite platforms. During the September 1998 cruise, backscattering coefficients were also acquired with a HOBI Labs Hydrosat 6 backscatter meter in collaboration with R. Maffione. Also, in the September cruise, a liquid capillary waveguide absorption spectrometer was field-tested in collaboration with Eurica D'Sa (NOAA/NESDIS). We hope to maintain these or other comparable collaborations in the

future, so that a complete suite of airborne and *in situ* optical measurements will continue to be obtained.

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PATENTS

Polymer Encapsulated Dual Emitters for Oxygen Sensing, Robert Pilato, Neil V. Blough, Kelly Van Houten and Danica Heath, University of Maryland Disclosure LS-98-047.